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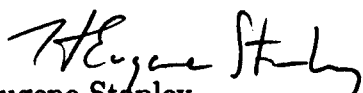
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"PHYSICS OF GELS WITH SHORT BOND LIFETIMES"

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Physics of Gels with Short Bond Lifetimes

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Final Report (1 October 1981 - 30 September 1987)

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Under the auspices afforded by this grant, we have made considerable progress on experimental approaches to the determination of water structure, and also in developing novel computer simulation techniques. We shall describe each of these in turn.

Statement A per telecon
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1. Raman Spectroscopy

NWW 4/30/92

1.1. Raman Spectroscopic Studies of OH Vibrations of Supercooled Water

We have performed detailed Raman spectroscopic measurements to study the structure of liquid water in the normal and supercooled temperature range. Experiments have been performed in the high frequency OH stretching vibration region and in the very low frequency intermolecular H-bond stretching vibration region (i.e., the hindered translational region). Our results from the high frequency region have shown that at low temperatures (0 to -20°C) most of the OH bonds are strongly H-bonded ($p_B \cong 0.9$) and that the distribution of the H-bond lengths and angles narrows as the temperature decreases; the rate at which the band width decreases with decreasing temperature is greater in the supercooled region than in the normal temperature region. The data also suggest that the local structure of water is tending towards a limiting structure as the limit of supercooling is reached. Locally it appears that this structure may be close to that of amorphous solid water.

1.2. H-Bond Stretching Vibrations: The Hindered Translational Region of Supercooled Water

The Raman data in the hindered translational region lend support to the results of Bosio-Teixeira-Stanley and Geiger-Stanley, that at low temperatures there exist small clusters of water molecules whose intermolecular motions are highly correlated. The fraction of these correlated clusters increases nonlinearly with decreasing temperature and the fine structure in the translational spectrum

suggests that these patches are tetracoordinated H_2O molecules. These results are reported in J. Chem. Phys. **79**, 5863 (1983).

1.3. Intermolecular Vibronic Coupling in Water

The question of the interpretation of the broad and complex Raman spectrum of liquid H_2O has been investigated in the context of intermolecular coupling. By obtaining the spectra of $\text{H}_2\text{O} + \text{D}_2\text{O}$ mixtures of varying composition (which produces HOD molecules), we have shown that as the concentration of HOD molecules increases, and thereby the probability of intermolecular vibronic coupling of neighboring OD oscillators increases, a low frequency band appears in the Raman spectrum. This band coincides with the low frequency feature seen in pure D_2O . The analysis of difference spectra clearly supports the idea that the spectrum of H_2O can be interpreted as arising from a strongly connected network of *one-dimensional* OH oscillators. These results are reported in J. Chem. Phys. **78**, 7132 (1983).

2. Small-Angle X-Ray Scattering

In collaboration with L. Bosio and J. Teixeira, we have made the first measurement of $S(q)$ at small scattering angles and low temperatures. Data can be fit by a Lorentzian line shape, with a characteristic half-width which corresponds to a length scale for density fluctuations of 8\AA . Perhaps coincidentally, 8\AA is the prediction of a theoretical picture of liquid water (developed by one of the PI's) which is based on the hydrogen bonding network properties of gels with short bond lifetimes.

3. Small-Angle Neutron Scattering

One of the PI's has made the first measurements of $S(q)$ at small angle and low temperatures using the complementary technique of neutron scattering (in collaboration with Pierre Chieux, John Dore, Louis Bosio, and Jose Teixeira). We used the D17 facility at ILL, Grenoble. Neutron data must be subjected to a thorough set of corrections before they can be interpreted, and the computer algorithms necessary for these correlations are currently being applied.

4. Low-Density "Patches" in the Hydrogen-Bonded Network of Liquid Water: Evidence from Molecular Dynamics Computer Simulations

We carried out detailed calculations of the local density fluctuations in liquid water, and found that density fluctuations are correlated with the degree of bondedness of a molecule. Specifically, we found that the hydrogen bond network includes many tiny spatially-correlated "patches" of four-bonded molecules, with the local density near a patch being lower than the global density. The diameter of these patches increases with decreasing temperature and is comparable to the characteristic length scale of density fluctuations that we had earlier measured by small-angle x-ray scattering. A preliminary report of this work was published in Physical Review Letters.

5. Tests of Universality of Percolation Exponents for a 3-Dimensional Continuum System of Interacting Waterlike Particles

We succeeded in obtaining the first estimates of percolation exponents for any interacting 3-dimensional continuum system—namely ST2 water, which was simulated with molecular dynamics. Our results were consistent with accepted values for ordinary random-bond percolation. Thus we have eliminated a major concern among many in the field of gel research, namely that it may be inappropriate to apply the random bond lattice percolation to describe interacting continuum systems, like polymer gels.

6. Gelation Models of Hydrogen-Bond Networks in Liquid Water

We obtained the first detailed information on cluster statistics of hydrogen bond networks in water using molecular dynamics. For small bond networks, the MD calculations agree well with the classic Flory theory, which neglects cycles. For larger networks, there is considerable disagreement. Therefore we carried out calculations using the connectivity of a four-coordinated ice lattice, which includes cycles and found much better agreement with the molecular dynamics data. Our work provides the first detailed molecular dynamics test of the range of validity of Flory theory in describing polyfunctional condensation network statistics.

7. Molecular Dynamics Calculations of the Raman, Infrared, and Inelastic Neutron Spectrum of Liquid Water

We have calculated the vibrational spectra of liquid water directly from molecular dynamics simulation. Our work represents the first attempt to directly simulate the vibrational motion starting with interactions between the H and O atoms in liquid water. The potential includes Lennard Jones interactions to represent the liquid state, Coulomb interactions to represent the H-bond network and Morse potentials to simulate the vibrations of the OH covalent bonds. All previous work in this area has been done with rigid molecules which do not include the vibrational potential. Thus, in the previous approach the vibrational spectrum has to be calculated by a separate normal coordinate analysis of few configurations generated from rigid molecule dynamics. In contrast, in our approach the trajectories of the molecular dynamics simulation also contain the vibrational motion and hence the vibrational spectrum can be directly obtained from appropriate correlation functions.

The calculated infrared, Raman, and neutron spectra are in excellent agreement with experiment and reproduce the correct temperature dependence.

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